

REMARKS/ARGUMENTS

Support for the amendment to Claims 1, 7, 8, 11, and 12 is found at specification page 3, lines 26-28. Support for new Claims 14-16 is found at specification page 3, lines 30-32. No new matter has been entered.

Applicants appreciate the withdrawal of the previously-applied rejection. New rejections have been made over the combination of Takehisa and Strebel. These rejections are traversed.

Applicant has attached hereto an English version of Takehisa (JP 04327582). This reference differs from the present claims in at least two ways: zeolite is not used as a catalyst, and the reference relies upon an alkyl hydroperoxide as the oxidizing agent, rather than hydrogen peroxide, as claimed.

Specifically, the catalyst in Takehisa is described in, e.g., paragraph [0012] at page 6 of the attached English version. Suggested for use are the acetylacetonate, alcoholate, naphthonate, etc. of metals such as molybdenum, tungsten, etc. Zeolites are not suggested. The oxidizing agent in Takehisa, alkyl hydroperoxide, is described in paragraph [0010] of the English version, where cumene hydroperoxide, ethylbenzene hydroperoxide, etc. are suggested. Hydrogen peroxide, as used in the present invention, is not suggested.

Interestingly, Takehisa does reduce the concentration of 1,5-hexadiene in reactant allyl chloride to 0.1 wt.% or less. The purpose of this purification is described in paragraph [0004] and [0005] of the English version: because olefinic compounds have similar properties to the product epichlorohydrin, it is better to remove such olefinic compounds from the starting materials rather than wait and try to remove them from the product epichlorohydrin. In addition, the presence of such olefinic impurities in the starting materials can produce hydrogenated products during reaction, again requiring expensive and difficult separation.

Thus, Takehisa describes the production of epichlorohydrin from allyl chloride and an alkyl hydroperoxide, not hydrogen peroxide, in the presence of a catalyst other than a zeolite, where 1,5-hexadiene has been removed prior to reaction in order to provide a more pure reaction product.

Strebel, the other reference used in the combination rejections, was co-authored by the first-named inventor of the present application. In Strebel epichlorohydrin is made by reacting allyl chloride with a peroxide compound in the presence of water, a catalyst and a diluent. See the paragraph bridging columns 1 and 2 of the reference. Zeolite catalysts can be used (column 2, lines 3ff) and the peroxide compound can include hydrogen peroxide (column 2, lines 29-31). The advance described in Strebel is the elimination of unwanted organochlorine products (column 1, lines 25-31).

Thus, the underlying reactions in Takehisa and Strebel are quite different from one another: different catalysts are used, and different impurities are removed. Accordingly, and due to the differences in the reaction schemes described, the references are not combinable. Even if the references are combined, there would be no reason to perform Takehisa's pre-reaction removal of 1,5-hexadiene in the Strebel process because Strebel focuses on chloro impurities, not olefin impurities, and because there would be no reason to expect that the different zeolite catalysts in Strebel would produce the undesirable hydrogenated products of the olefinic impurities that are produced by the Takehisa catalysts. See paragraph [0005] of Takehisa.

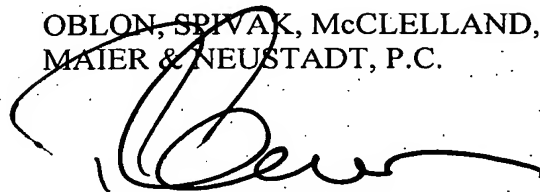
Moreover, and just as importantly, even if one were to selectively combine various portions of the Takehisa and Strebel disclosures to provide the present invention, there would be absolutely no expectation of an improvement in zeolite catalyst life. This improvement has been amply demonstrated in the present specification, and is of course extremely commercially important.

Whenever a catalyst lasts longer, it need not be changed as often, production need not be stopped as often, and more product can be made in a given amount of time. As shown in the Examples beginning at page 7 of the present specification, when zeolite catalysts are used and the allyl chloride is free of 1,5-hexadiene according to the present claims (a combination nowhere provided in any single reference applied) a dramatic and sustained improvement in catalyst life and, consequently, degree of conversion, is obtained. For example, and as shown in Table 1 at specification page 7, production using normal allyl chloride is exhausted at 27 hours, while allyl chloride according to the present invention remains active at 147 hours of reaction time. Similar results are shown in Tables 2 and 3, all of which show an impressive extension of catalyst life and conversion percent. Because neither Takehisa, Strebel, nor their combination disclose or suggest such an advantage, even if the references could be combined in a manner such that the present claims were suggested, which they cannot, Applicants' invention still would be patentable in view of their demonstration of superior results.

Accordingly, and because the references, even when combined, fail to suggest the present invention, and because Applicants have shown significantly superior results and an important advantage undisclosed by any applied reference, Applicants respectfully request the reconsideration and withdrawal of the outstanding rejections, and the passage of this case to Issue.

Respectfully submitted,

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**(54) [Title of the Invention]**

A method for the production of epichlorohydrin

**(57) [Abstract]**

[Constitution] In a method for the production of epichlorohydrin from allyl chloride and an alkyl hydroperoxide in the presence of catalyst, the allyl chloride is employed in the reaction after reducing the concentration of 1,5-hexadiene contained therein.

[Effects] In the product purification stage, there is no need to carry out further reaction or the like for the purposes of eliminating trace impurities from the epichlorohydrin of enhanced concentration, and so it is possible to obtain highly pure epichlorohydrin easily merely by a distillation operation.

**[Scope of Claim]**

[Claim 1] A method for the production of epichlorohydrin which is characterized in that, in a method for the production of epichlorohydrin from allyl chloride and an alkyl hydroperoxide in the presence of a catalyst, the allyl chloride is employed in the reaction after reducing the concentration of 1,5-hexadiene contained therein to 0.1 wt% or less.

**[Detailed Description of the Invention]**

[0001]

[Industrial Field of Application] The present invention relates to a method for the production of epichlorohydrin.

[0002]

[Prior-Art] With regard to the methods for synthesizing epichlorohydrin by the reaction of allyl chloride and an alkyl hydroperoxide in the presence of a molybdenum, tungsten, titanium, tantalum, niobium, vanadium, zirconium or boron compound catalyst, as examples of known methods where a homogeneous catalyst is used there are those in JP-B-48-19609 and JP-B-45-17649, and as examples of known methods employing a heterogeneous catalyst there are those in West German Patent 2334315, US Patent 4021454, Journal of Catalysis 31, 438 (1973), JP-A-52-7908 and JP-B-54-40526, and also the method disclosed by the present inventors in JP-A-64-257701.

[0003] In a typical process for the recovery of the epichlorohydrin from the reaction mixture obtained by these methods, first of all the excess allyl chloride is driven off by distillation and the epichlorohydrin recovered in the residual liquid, after which the epichlorohydrin and the alcohol which is the reduction product of the alkyl hydroperoxide used are respectively separated and recovered from the heavy material and said alcohol reduction product of the alkyl hydroperoxide. The distilled allyl chloride is re-supplied to the reactor, and the alcohol which is the reduction product of the alkyl hydroperoxide used is either recovered as it is, or it is converted to an olefin by a dehydrocondensation reaction, and then transformed to the alkyl hydroperoxide via hydrogenation and oxidation reactions, for re-use in the reaction with the allyl chloride.

[0004] For the separation and recovery of the epichlorohydrin, normally a distillation process is used but, commercially, a highly pure epichlorohydrin product is demanded and the elimination of impurities is essential. In particular, the introduction of olefinic compounds considerably lowers the value of the epichlorohydrin product. However, some olefinic compounds resemble epichlorohydrin in physical properties, so elimination is not possible by an ordinary distillation process. As a method for selectively removing the olefinic compounds from epichlorohydrin, there is disclosed in JP-B-63-46752 a method in which a hydrogenation treatment of the olefinic compounds is carried out in the presence of a palladium catalyst.

[0005]

[Problems to be Resolved by the Invention] However, in this method an expensive catalyst is required and, furthermore, since hydrogenated products of the olefinic compounds are produced or since new by-products may be produced such as for example conversion of epichlorohydrin to alcohol during the hydrogenation of the trace olefinic compounds present in the epichlorohydrin, further distillation equipment becomes necessary for the removal of these.

[0006]

[Means for Resolving the Problems] The present inventors have carried out a painstaking investigation to resolve the aforesaid problems, as result of which they have perfected the present invention. That is to say, the epichlorohydrin production method of the

present invention is characterized in that, in a method for the production of epichlorohydrin from allyl chloride and an alkyl hydroperoxide in the presence of catalyst, the allyl chloride is employed in the reaction after first reducing the concentration of the 1,5-hexadiene contained therein to 0.1 wt% or less.

[0007] In the present invention, in the reaction between the allyl chloride and the alkyl hydroperoxide in the presence of catalyst, the concentration of the 1,5-hexadiene contained in the allyl chloride is reduced beforehand to 0.1 wt% or less, and so it is possible to produce highly pure epichlorohydrin by an ordinary distillation process.

[0008] The allyl chloride referred to in the present invention is itself produced by the hot chlorination or oxychlorination of propylene and, as chief impurities, there are usually contained 0.3-0.5 wt% of 1,5-hexadiene and 0.3-0.5 wt% 1-chloropropane. Of these, the 1-chloropropane is essentially not converted to other materials in the reaction with the alkyl hydroperoxide, so separation from the epichlorohydrin is easy. However, 1,5-hexadiene is readily epoxidized in the reaction with the alkyl hydroperoxide and converted to 1,2-epoxy-5-hexene, which is difficult to separate from epichlorohydrin.

[0009] Thus, in the present invention, the 1,5-hexadiene is separated from the allyl chloride by a distillation process prior to use of the allyl chloride in the reaction. The distillation equipment and the operational method are not particularly restricted, and the distillation can be carried out either on a

batchwise basis or continuously, provided there are employed operational conditions and a distillation column having the number of theoretical plates such that the 1,5-hexadiene may be separated. However, if the pressure is too low in reduced-pressure distillation, a considerable amount of energy is required for the condensation cooling of the allyl chloride and light materials, so this is uneconomic. While it is most desirable that there essentially be no 1,5-hexadiene present in the distilled and purified allyl chloride, the concentration should be no more than 1,000 ppm and more preferably no more than 500 ppm.

[0010] The alkyl hydroperoxide employed will be cumene hydroperoxide, ethylbenzene hydroperoxide, tert-butyl hydroperoxide or cyclohexyl hydroperoxide and, optionally, the alkyl hydroperoxide may be employed diluted with solvent. As examples of the solvent used for dilution, there are those present as unreacted starting materials from the production of said alkyl hydroperoxide, such as cumene or ethylbenzene, those produced from the alkyl hydroperoxide such as dimethylphenylcarbinol, phenylcarbinol or tert-butyl alcohol, and also chlorinated organic compounds such as chlorobenzene.

[0011] With regard to the molar ratio of the allyl chloride to the alkyl hydroperoxide in the present invention, it is preferred that the allyl chloride be present in excess and, normally, there is 1.1-50 mol, and more preferably 2-20 mol, thereof per 1 mol of the alkyl hydroperoxide. If there is less than 1 mol, then an adequate yield of the epichlorohydrin is not obtained, while with more than 50 mol a considerable amount of

energy is consumed in the recycling of starting materials, so this is uneconomic.

[0012] The catalyst in the present invention is an acetylacetonate, alcoholate, naphthionate, chloride, oxide or carbonyl compound of molybdenum, tungsten, titanium, tantalum, niobium, vanadium, zirconium or boron, and it may or may not be a compound which dissolves in the starting material solution. Furthermore, the catalyst may be used in a form held on a solid support such as silica gel, alumina or zirconia. It is also possible to jointly employ two or more of these catalysts. Again, in addition to the catalyst, a basic substance such as n-butylamine, triethylamine or magnesium oxide may also be present in the reaction liquid. The amount of catalyst employed is not particularly restricted but the amount of metal in the catalyst, in terms of the alkyl hydroperoxide used, is preferably 0.01 to 2 mol%, and more preferably 0.1 to 1 mol%. With less than 0.01 mol, a sufficient yield of the epichlorohydrin is not obtained, whereas more than 2 mol is uneconomic. The reaction can be carried out as a batch reaction or as a continuous flow reaction. The reaction temperature is 0 to 150°C and more preferably 20 to 120°C. At less than 0°C, the reaction is slow and at more than 120°C decomposition of the alkyl hydroperoxide takes precedence.

[0013]

[Examples] Below the present invention is explained in more specific terms by means of examples.

[0014] Example 1

(Purification of the allyl chloride) Using a Helipak-filled column type batch distillation device having 10 theoretic plates, distillation was carried out under conditions comprising normal pressure, 46°C and a reflux ratio of 10. Allyl chloride of composition as shown in Table 1 was obtained.

[0015]

[Table 1]

Component	Before Purification	After Purification
1,5-hexadiene	0.400 wt%	0.005 wt%
1-chloropropane	0.442 wt%	0.440 wt%
allyl chloride	99.108 wt%	99.509 wt%
others	0.050 wt%	0.046 wt%

(Preparation of the Catalyst) 120 ml of anhydrous ethanol plus 2.38 g of titanium tetrachloride were added under a nitrogen gas seal to a flask equipped with a stirrer, and then stirring carried out for 30 minutes. Next, 60 g of silica gel was added and stirring performed for 60 minutes, after which the ethanol was distilled off at normal pressure and then drying carried out for 1 hour at 100°C under reduced pressure, followed by 2 hours firing in a current of air at 200°C. The material obtained, which comprised titanium supported on silica gel, was introduced under a nitrogen seal along with 7.46 g of 1,1,1,3,3,3-hexamethyldisilazane into an autoclave equipped with a stirrer, heated for 4 hours at 200°C and the catalyst obtained.

[0016] Next, while mixing 17 g of the aforesaid catalyst and 17 g of magnesium oxide, they were packed

into a pressure-resistant glass reaction tube of internal diameter 20 mm and length 300 mm which was provided with a heating jacket, and a 44 wt% cumene solution of cumene hydroperoxide plus the purified allyl chloride obtained in Example 1 were passed continuously from the bottom of the reaction tube at a weight ratio of 8 : 20 per hour. The heating jacket temperature was adjusted so that the temperature of the packed layer was maintained at 90°C. When the reaction mixture obtained after 64 hours was analysed by means of gas chromatography, it was found to have the composition shown in Table 2.

[0017]

[Table 2]

Component	Concentration
epichlorohydrin	6.22 wt%
dimethylphenylcarbinol	12.01 wt%
cumene hydroperoxide	0.76 wt%
cumene	14.41 wt%
1,2-epoxy-5-hexene	no more than 10 ppm
allyl chloride, etc	66.60 wt%

After distilling-off the allyl chloride from this reaction mixture, the residual liquid was subjected to rectification under conditions of 60°C temperature, 100 Torr pressure and reflux ratio 10, and the epichlorohydrin recovered. When the recovered material was analyzed by gas chromatography, no 1,2-epoxy-5-hexene was detected.

[0018] Example 2

1,5-hexadiene was added to the allyl chloride following purification in Example 1, to prepare allyl chloride of composition shown in Table 3.

[0019]

[Table 3]

Component	Concentration
1,5-hexadiene	0.035 wt%
1-chloropropane	0.440 wt%
allyl chloride	99.479 wt%
other	0.046 wt%

Using this allyl chloride, reaction was carried out using the same catalyst and the same reaction equipment as in Example 2 (sic), and when the epichlorohydrin was distilled and recovered there was found to be 0.07 wt% of 1,2-epoxy-5-hexene present.

[0020] Comparative Example 1

Using the allyl chloride in Example 1 prior to purification, reaction was carried out employing the same catalyst and the same reaction equipment as in Example 2. When the reaction mixture obtained after 40 hours was analyzed by gas chromatography, the composition was as shown in Table 4.

[0021]

[Table 4]

Component	Concentration
epichlorohydrin	6.25 wt%
dimethylphenylcarbinol	12.18 wt%
cumene hydroperoxide	0.73wt%
cumene	14.48 wt%
1,2-epoxy-5-hexene	0.09 wt%
allyl chloride, etc	66.27 wt%

After distilling off the allyl chloride from this reaction mixture, the residual liquid was subjected to rectification under conditions of 60°C temperature, 100 Torr pressure and reflux ratio 10, and the epichlorohydrin recovered. When the recovered material was analysed by gas chromatography, it was found that there was 1.14 wt% of 1,2-epoxy-5-hexene present.

[0022]

[Effects of the Invention] By the method of the present invention, there is no longer any need to carry out a further reaction, etc, in order to eliminate trace impurities from the epichlorohydrin of enhanced purity in the product purification stage, and so it is possible to obtain highly pure epichlorohydrin readily merely by a distillation process. Thus, the method is extremely valuable industrially.